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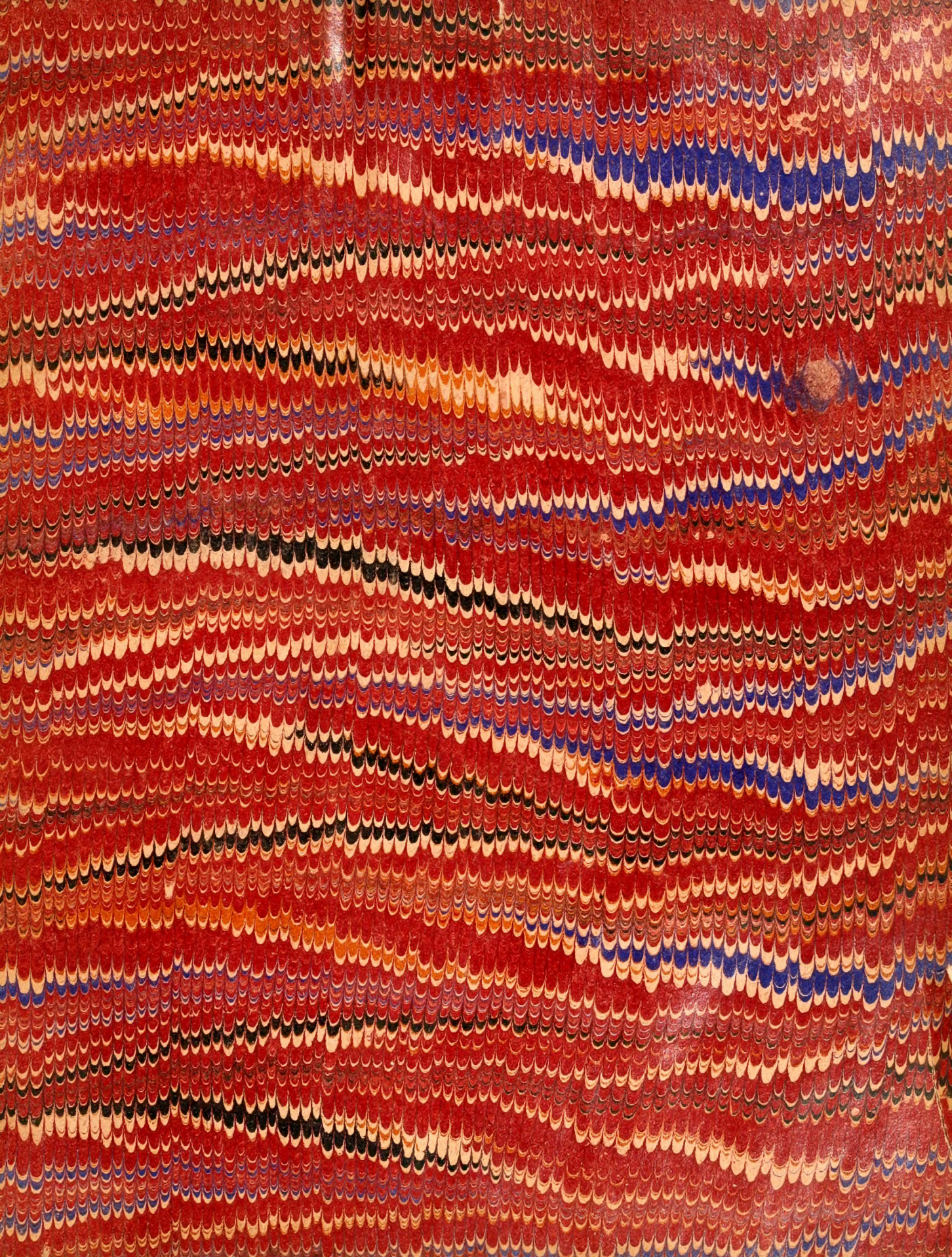
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Sonic Double Chlorides

BISPHUTH

Some Double Chlorides

CONTAINING

BISMUTH

A DISSERTATION

ON THE  
NATURE AND PROPERTIES OF  
THE DOUBLE CHLORIDES OF  
BISMUTH AND ARSENIC

BY

C. P. H. E. RICHARD.

1831



# Some Double Chlorides

CONTAINING

## BISMUTH.

A DISSERTATION

PRESENTED TO THE BOARD OF UNIVERSITY STUDIES  
OF THE JOHNS HOPKINS UNIVERSITY FOR  
THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

C. PLINY BRIGHAM.

1891



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## Acknowledgment

I desire to offer my most sincere thanks to Professor Kinsen at whose suggestion and under whose immediate direction the following investigation has been carried out.

I wish also to thank Doctors Morse and Penouf for valued instruction, and finally Doctor George H Williams under whom the course in mineralogy and geology was pursued.

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## Introduction.

It was for a long time held that a sharp line could be drawn separating the oxygen acids and bases, but as experiments have shown, some substances have the power to act in either capacity, depending on the way they are treated.

Chromium for example: when Chromium hydroxide is treated with hydrochloric acid, a chloride is formed, with Chromium performing the function of a base, while when treated with alkaline hydroxides, a chromite results, here Chromium shows acid properties.

Many of basic oxides and acidic oxides unite to form salts, should not the





halides unite to form compounds in keeping in constitution to the double oxides?

Not only, why should they not be formed, but why should they not occur in places in text rocks with significant names? Thus  $K_2O + SO_3 = K_2SO_4$  or potassium sulphate is given in all rocks as a derivative of the well known sulphuric acid; while a salt formed by potassium chloride and lead chloride is generally disregarded entirely because the acid from which it is most likely derived does not exist in the free state, namely chloro-plumbous acid

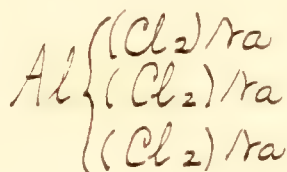
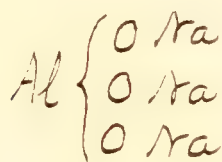
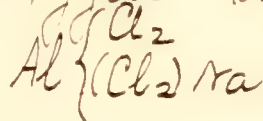
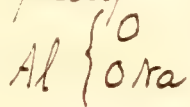
$KCl + PbCl_2 = KPbCl_3$  or potassium chloro-plumbite

in a paper in 'Engl. Review' entitled "On the Nature and Structure of the double

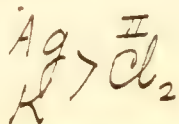




halides". He emphasizes the point — the close similarity between the double oxides or oxygen salts, and the double halides, the act involved in their formation and for their explanation suggests that "two halogen atoms together can play the same part that the <sup>o</sup> is called linking oxygen atoms plays in the oxygen salts" Thus:



This view has been held for many years. The same explanation was first offered by Naquet<sup>2</sup> in 1867; he says in the compound of silver chloride and potassium chloride the chlorine acts as a bivalent element and gives to the formula

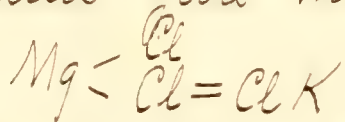


<sup>2</sup> Principes de Chimie fondée sur les théories modernes.  
Par A. Naquet. Paris, 1867.





Blomstrand<sup>3</sup> 1869 offers a similar explanation for the double chloride of magnesium and potassium and gave this formula



in which he conceives the chlorine atom to be a trivalent element.

At this view that halogen atoms can play the same part as uniting oxygen atoms, it is easy to see the very close analogy existing between the ordinary oxygen salts and the double halides.

Prof. Remsen, after an exhaustive examination of the composition of this large class of compounds, deduces this law.

"When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater."

<sup>3</sup> Die Chemie der Jetztzeit vom Standpunkte der elektro-chemischen Auffassung aus Berzelius' Lehre entwickelt.





and is generally less than the number of halogen atoms contained in the latter". The principal objection to this view is by Prof. Horstmann<sup>4</sup> and based on the valence of the halogen — that they are univalent — granting this, what would become of the well established compounds  $\text{ICl}_3$  and  $\text{IF}_3$ ? if it be granted that these are true chemical compounds, then the objection of Prof. Horstmann loses force.

A few words regarding the double halides of bismuth and the alkalis will not be out of place in this connection. With potas-

$\text{BiCl}_3 \cdot 3\text{KCl}$	Arbce	Bergelius	brichter	25, 279
$\text{BiCl}_3 \cdot 2\text{KCl}$	"	"	"	25, 279
$\text{BiCl}_3 \cdot 2\text{KCl} + 2\text{H}_2\text{O}$	Jacqueline	Ann. Chim. Phys.	00, 113	
$\text{BiI}_3 \cdot 2\text{KI} + \text{H}_2\text{O}$	Arbce	Bergelius	Jahrb.	25, 284
$\text{BiI}_3 \cdot 4\text{KI} + \text{HI} (?)$	"	"	"	25, 284

4-Lehrbuch der Physikalischen und Theoretischen Chemie  
von A. Horstmann und H. Landolt.





$\text{BiCl}_3 \cdot 2\text{KBr} + 1/2\text{H}_2\text{O}$  Atkinson *T. Chem. Soc.* 1883, 292  
 Of the double potassium-bismuth salts I  
 worked only with the chlorides. The result  
 of this investigation proved the non-existence  
 of the salts  $\text{BiCl}_3 \cdot 3\text{KCl}$  and  $\text{BiCl}_3 \cdot 2\text{KCl}$   
 obtained by Arppe, while under certain  
 conditions a compound of the composition  
 $\text{BiCl}_3 \cdot \text{KCl} + \text{H}_2\text{O}$  was formed, of which I  
 can find no record.

There are recorded many other double hal-  
 ides of bismuth, which are here tabulated  
 with their respective references:

$\text{BiCl}_3 \cdot 2\text{NaCl} + 3\text{H}_2\text{O}$	Jacqueline	<i>Ann. chim. phys</i>	66, 113
$\text{BiCl}_3 \cdot \text{NH}_4\text{Cl}$	"	"	" 66, 113
$\text{BiCl}_3 \cdot 2\text{NH}_4\text{Cl}$	Deherain,	<i>Compt. rend.</i>	54, 724
$\text{BiCl}_3 \cdot 3\text{NH}_4\text{Cl}$	"	"	" 54, 724
$\text{BiBr}_3 \cdot 3\text{NH}_4\text{Cl} + \text{H}_2\text{O}$	Muir	<i>T. Chem. Soc.</i>	1876, 148
$\text{BiBr}_3 \cdot 2\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$	"	"	" 1876, 148
$\text{BiBr}_3 \cdot 2\text{NH}_4\text{Cl} + 5\text{H}_2\text{O}$	Nickles	"	" 1876, 148



2 BiBr<sub>3</sub> 5/11 HCl + 11 H<sub>2</sub>O Ann. Chem. Soc. 1877, 28.

Of other double salts of bismuth there are two of the composition

3 K<sub>2</sub>SO<sub>4</sub> · Bi<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> Berzelius Jahrb. 25, 286

2 K<sub>2</sub>SO<sub>4</sub> · BiO(SO<sub>4</sub>)<sub>2</sub> " " 25 286

I speak of these simply because in a method of analysis employed for the determination of chlorine in the double chloride BiCl<sub>3</sub> · 2 KCl + 2 H<sub>2</sub>O I obtained a salt - a double sulphate - differing in composition from either of the above and mentioned of which I have been unable to find in the literature.

Godeffroy<sup>5</sup> describes the salts BiCl<sub>3</sub> · 6 KCl and BiCl<sub>3</sub> · 6 LiCl, which cannot but strike one as being marked exceptions to Prof. Berzelius' law. With these facts at hand the following work on the double salts of bismuth chloride with the chlorides of antimony and

<sup>5</sup> Berichte 8, 9 und Zeitschrift des allgemeinen österreichischen Apotheker-Vereins





caesium was undertaken to determine whether or not these compounds really exist. At the time Prof. Remsen's article appeared the following salts were found described in the literature and appear as exceptions to the rule

$\text{SnCl}_2.4\text{KCl}+3\text{H}_2\text{O}$	Poggiale, J. prakt. Chem. 35, 329
$\text{CuCl}_2.2\text{KCl}$	mitochevich, Ann. chim. phys. 73, 384
$\text{MnCl}_2.7\text{H}_2\text{O}$	Meitner, Bull. Soc. Chim. [2] 8, 408
$\text{PbCl}_2.7\text{H}_2\text{O}$	Boullay, Ann. chim. phys. [2] 34, 370
$\text{BiCl}_3.5\text{KCl}$	Godéron Berichte 8, 0
$\text{BiCl}_3.5\text{CsCl}$	" " 8, 0
$\text{SbCl}_3.6\text{RbCl}$	" " 8, 9
$\text{SbCl}_3.5\text{LiCl}$	" " 8, 0

$\text{CdCl}_2.4\text{KCl}$  von Hauer Meina Akad. ber 15, 23  
 For the past two years work has been carried on along this line, in this laboratory with the most gratifying results, as many of these salts have been shown not to exist.





Mr C. H. Hertig<sup>6</sup> has most carefully investigated the double salts of lead and potassium with the results — that none of those salts which appear as exceptions exist, but the compound  $KPbI_3 + 2H_2O$  is always formed when lead iodide and potassium iodide are brought together in hydrochloric acid solution.

Mr Geo M. Richardson<sup>7</sup> in his work on the double salts of Sn and potassium shows conclusively that the compound  $SnCl_2 \cdot 4KCl \cdot 3H_2O$  as described by Poggiale cannot be obtained.

Mr C. E. Saunders also working in this laboratory has been unable to obtain either of the salts  $SnCl_2 \cdot 6KCl$  or  $SnCl_2 \cdot 6CsCl$ .

Christensen<sup>8</sup> shows that the salt  $PbCl_2 \cdot 7KCl$  cannot be prepared according to the directions given by Nickles.

With the results of the work described in the following pages, all the exceptions to the law

<sup>6</sup> Thesis for Ph.D. degree Johns Hopkins University 1890

<sup>7</sup> J. prakt. Chem. 1886, 4

<sup>8</sup> J. prakt. Chem. 1886, 4



have been explained away, save the compounds  $\text{CuCl} \cdot 2\text{KCl}$  and  $\text{CdCl}_2 \cdot 4\text{KCl}$ . All work on these latter two points to the correctness of these formulae as expressing their true composition.

---





## Method of Analysis.

Although Godeffroy in his article gives the results of complete analyses of the different salts described therein, he fails to give the methods employed, which would indicate, to say the least, that they are simple and straightforward; but the work of analysing the double chlorides of bromine and the alkalis present many difficulties; a few of which I will cite.

Ammonium sulphide (freshly prepared) was added to the double salt to which water had previously been added - this precipitates the bromine, which was filtered off in a washed filter, washed with water containing a little hydrogen sulphide, dried in an air





bath at  $90^{\circ}$ , scraped into a weighed porcelain crucible (the filter afterward omitted) and treated with a few drops of P.P. nitric acid. The lid to the crucible being in place so as to avoid loss by spattering.

The contents of the crucible was evaporated to dryness over a water bath, heated to constant weight by a Bunsen burner and finally over a blast lamp; the resulting oxide thus obtained melting without loss in weight.

To determine the chlorine in the filtrate, it was first necessary to remove the excess of ammonium sulphide; to do this cadmium nitrate free from arsenic was added, whence cadmium sulphide came down. Copper sulphate was first used, but copper sulphide being soluble in ammonium sulphide, ~~it~~ would not answer. After filtering off the cadmium



sulphide, a little nitric acid and silver nitrate was added; the results obtained in this way, were always 4 or 5 percent low; this error arises from the fact that when ammonium sulphide is used to precipitate the bismuth 'insides' the sulphide, some oxychloride comes down.

It was hoped that by dissolving the double salt in a little nitric acid and then adding a sulphide this trouble could be overcome, but if this is done a large amount of sulphur is thrown out with the bismuth sulphide, which seriously interferes with the determination of bismuth.

After several months more the following method was found to be satisfactory.

A weighed portion of the salt not more than .2 gram was treated with water and a little C.P. hydrochloric acid and heated.





nearly to boiling (There should be enough acid<sup>to</sup> prevent the formation of any basic bromine salts). Sulphuretted hydrogen was then passed in until the supernatant liquid becomes clear; the bromine sulphide thus formed is filtered off on a quantitative filter, and washed with water containing a little hydrogen sulphide, dried, transferred to a weighed porcelain crucible, heated with CP nitric acid, evaporated to dryness and heated to a constant weight by a Bunsen burner and finally over a blast lamp; bromine is calculated from the oxide thus obtained.

Besides determining bromine as the oxide I also determined it directly from the sulphide by filtering this through a given crucible, and drying it at  $100^{\circ}$  to constant weight.

Both of these methods give good results.



To determine the alkali, the filtrate is evaporated to dryness, dissolved again in a little water, filtered into a weighed platinum crucible, evaporated to dryness on a water bath, and then heated for 2 hours at  $235^{\circ}$  in an air bath and when cool weighed [in the case of caesium it was only heated to about  $170^{\circ}$ ]; the crucible is then heated for a few seconds only on a Bunsen burner to a dull red heat and again weighed - the loss here is generally less than .4 mg.

To make the results more accurate the alkali thus determined as the chloride, must be dissolved in a little hot water and filtered, the filter burnt and weighed thus any insoluble matter present, such as silicates, from the glass vessels used in evaporation, can be detected, and then might be subtracted from





The weight of the alkali obtained. This method gives good results.

To determine Chlorine — A second sample of the salt is dissolved in several cubic centimeters of C.P. nitric acid, free from chlorine, and water, this is then heated almost to boiling, when about 15 c.c.s more of C.P. nitric acid are added — This large excess of acid is necessary to prevent the formation of any basic bromide salts. —

The chlorine is then precipitated by a not too weak solution of silver nitrate. The silver chloride was filtered off in a Gooch crucible, first washed with water containing nitric acid and finally with water alone.

The results for chlorine obtained in this way are entirely satisfactory.



## Di-potassium Chloro-bismuthite



Arppe describes a salt  $K_3BiCl_6$  ( $BiCl_3 \cdot 3KCl$ ) and states when 3 atomic weights of bismuth oxide are dissolved in hydrochloric acid and 2 atomic weights of potassium chloride are added, on evaporation rhombic crystals separate out, which on analysis can be shown to have the composition  $K_3BiCl_6$ .

Following these directions closely I obtained beautiful four sided crystals with two opposite angles cut off thus presenting a six-sided appearance; the analysis of this salt showed it to have the composition  $BiCl_3 \cdot 2KCl \cdot 2H_2O$ .

The results obtained are here given.

.1421 gram salt gave .0659 gram  $Bi_2O_3$  = .05907 gram Bi.





.1472 gram salt gave .2115 gram  $\text{AgCl}$  = .0522828 gram Cl  
.1419 " " " .0417 "  $\text{KCl}$  = .02187582 " K  
.1025 " " lost .0074 grams  $\text{H}_2\text{O}$

Calculated for  
 $\text{BiCl}_3 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$

Found

Bi	41.63	41.57
K	15.66	15.49
Cl	35.48	35.51
$\text{H}_2\text{O}$	7.20	7.18

This salt is stable in the air. It does not lose its water of crystallization in a desiccator, but when heated to  $100^\circ$  becomes anhydrous. It dissolves in moderately concentrated hydrochloric acid and can be recrystallized from the same without any change in composition. Its crystallizing power is very great.

All attempts to get the salt with three molecules of potassium chloride were fruitless;



chromium oxide and potassium chloride were mixed in the exact proportions; one of the former to six of the latter, yet the only salt obtained was  $K_2BiCl_5 \cdot 2H_2O$ .

Again a large excess of potassium chloride was used and under these conditions potassium chloride crystallizes out first and then the double salt with 2 molecules of the alkali chloride.

Hence I feel justified in asserting that no salt of the formula  $K_3BiCl_6 \cdot 2H_2O$ . Although no description of a double salt of chromium and potassium chloride, containing less than two atoms of potassium to one of chromium, could be found an investigation on this point was made when a salt of the composition  $KBiCl_4 \cdot H_2O$  ( $BiCl_3 \cdot KCl \cdot H_2O$ ) was obtained.





# Mono-potassium Chloro-bismuthite.



When  $2\frac{1}{2}$  atomic weights of bismuth oxide are dissolved in hydrochloric acid and 2 atomic weights of potassium chloride are added and the solution evaporated to a syrupy consistency, there crystallize out rain-fine fibre-like needles radiating from centres.

If the solution was not concentrated sufficiently by evaporation the salt  $\text{K}_2\text{Bi}_2\text{Cl}_6 \cdot 2\text{H}_2\text{O}$  invariably crystallized out.

The analysis of this salt dried first by means of a porous plate, and then between filter papers, gave these results:

I	.4109 gram salt gave .2338 gram $\text{Bi}_2\text{O}_3$ = .2090017 gram Bi
II	.1758 " " " .1005 " $\text{Bi}_2\text{O}_3$ = .090098 " Bi
III	.1910 " " " .1095 " $\text{Bi}_2\text{O}_3$ = .09816675 " Bi



$\text{..910 gram salt gave .0303 gram Cl} = .0190 \text{ gram K}$   
 $\text{.1753 " " " .0324 " KCl} = .016998 \text{ " K.}$

$\text{..752 gram salt gave .2503 gram AgCl} = .06187416 \text{ gram Cl.}$   
 $\text{.2082 " " " .2976 " AgCl} = .0735667 \text{ " Cl.}$

$\text{..709 gram salt lost .0190 gram H}_2\text{O.}$   
 $\text{.45405 " " " .0167 " H}_2\text{O.}$

Calculated for		Found		
$\text{BiCl}_3 \cdot \text{KCl} \cdot \text{H}_2\text{O}$		I	II	III
Bi	51.11	51.01	51.25	51.39.
K	9.62	9.96	9.66	—
Cl	34.85	35.31	35.32	—
H <sub>2</sub> O	4.43	4.52	—	3.67.

The sample of salt used in analysis III was made from a solution containing a very large excess of bismuth chloride which readily accounts for the high percentage gotten for bismuth and the low percentage





for water.

This salt is stable in the air; it cannot be recrystallized except from a strong solution of potassium chloride which prevents staining the salt entirely free from potassium chloride. When dissolved in hydrochloric acid on recrystallizing it goes over into  $K_2B_2O_5 \cdot 2H_2O$  which appears to be the most stable of the double chlorides of boron and potassium.

This salt ( $KB \cdot Cl_4 \cdot H_2O$ ) when placed in a desiccator over chloride of calcium loses one-half of its water, while the remainder cannot be driven off below  $100^\circ$ .

Weight of the tub + salt (dried on a porous plate)	= 8.870,94
" " " Empty	= 8.859,2 "
" " " salt	= .7109 "
" " " tub + salt dried to const wgt in desiccator	= 8.8608 "
" " " " + " heated " " " at $105^\circ$	= 8.8515 "



Loss in weight of salt dried at  $105^{\circ} = .0186 \text{ gr}$

" " " " in a desiccator = .0093 "

percentage of water lost by drying in a desiccator  
= 2.26

percentage of water in the salt when heated  
to constant weight at  $105^{\circ} = 4.52$  ; thus it  
appears that in the salt dried over calcium  
chloride there is  $\frac{1}{2}$  molecule of water of  
crystallization.

A sample of this salt was heated to  $140^{\circ}$   
but the loss in weight indicated the pres-  
ence of but one molecule of water ; when  
a higher temperature was tried the  
salt underwent a slight decomposition.



21

Potassium-bismuth Alum.



In trying to overcome the difficulties of analyzing the double chloride for chlorine, a method was tried which unexpectedly yielded the salt  $KBi(SO_4)_2$ .

A weighed quantity of the double chloride of bismuth and potassium was placed in an erlenmeyer flask and treated with concentrated sulphuric acid - the hydrochloric acid set free being conducted into a dilute solution of sodium hydroxide, in this way I hoped to obtain good results on chlorine, but failed. However after heating the contents of the flask for several hours, on cooling I noticed fine needle-shaped crystals; on the addition of water they





dissolved and by evaporation were deposited in the needle form as well as in beautiful glistening plates.

The analysis of these crystals show them to have the composition  $[\text{K}_2\text{SO}_4 \cdot \text{Bi}_2(\text{SO}_4)_3]$  or  $\text{KBi}(\text{SO}_4)_2$  analogous to our ordinary alum  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . As is to be expected this salt has no water of crystallization being formed in concentrated sulphuric acid.

These are the results obtained:

.3478 gram salt gave	.1841 gram $\text{Bi}_2\text{O}_3$	= .1650056 gram Bi
.2081 " " "	.1109 " $\text{Bi}_2\text{O}_3$	= .0994218 " Bi

.2081 gram salt gave	.5416 gram $\text{K}_2\text{SO}_4$	= .5186817 gram K
.2088 " " "	.0477 " $\text{K}_2\text{SO}_4$	= .021455 " K

.3478 gram salt gave	.3672 gram $\text{BaSO}_4$	= .151139 gram So <sub>4</sub>
.1248 " " "	.1337 " $\text{BaSO}_4$	= .055031 " So <sub>4</sub>



Calculated for		Found	
$K(Bi(SO_4)_2$		I	II
Bi	47.36	47.44	47.77
K	8.91	8.99	8.98
SO <sub>4</sub>	43.72	44.10	43.72

The method of analysis is as follows:  
 dissolve a weighed quantity of the salt in water and hydrochloric acid, add barium chloride to precipitate all the sulphuric acid as barium sulphate — there must be enough hydrochloric acid present to prevent the formation of any basic bismuth salts — filter off into a good crucible the barium sulphate, wash first with dilute hydrochloric acid and finally with water dry and weigh, thus calculating the SO<sub>4</sub>.

In the filtrate the bismuth can be determined if not too much acid is present, or a new sample dissolved in water and hydrochloric acid will suffice, in this





case the determination is exactly the same as with the double chlorides.

To determine the potassium a third sample is dissolved as before, hydrogen sulphide passed in to precipitate the iron which is filtered off, and the filtrate evaporated to dryness, redissolved, and filtered into a weighed platinum dish, and again evaporated to dryness, add 3 or 5 drops of sulphuric acid and heat to dryness over a free flame the acid salt first formed being transformed finally in  $H_2SO_4$  from the weight of which the potassium is calculated.

This salt possesses the remarkable property of being quite insoluble in cold water, on boiling it however it decomposes into a basic borate sulphate of the composition  $B_2O_3 \cdot 2H_2O$ . A quantity of the salt  $K(BSO_4)_2$  was boiled in water and the insoluble part filtered off and



dried on a porous plate and analyzed with the following results:

.0896 gram salt gave .0717 gram  $\text{Bi}_2\text{O}_3$  = .064279 gram Bi  
 .0896 " " " .0357 "  $\text{BaSO}_4$  = .014694 "  $\text{SO}_4$  ~~Bi~~

calculated for  
 $\text{Bi}_2\text{O}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$

Found

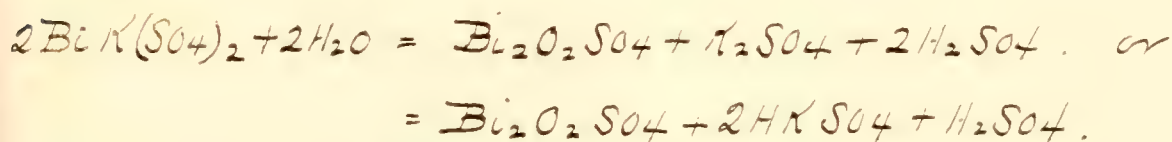
Bi 71.72

71.74

$\text{SO}_4$  16.55

16.39.

In the filtrate was found potassium and sulphuric acid hence the decomposition may be expressed thus



### Potassium-antimony Alum.

By analogous methods of work I hoped to have obtained a double sulphate of antimony



and potassium as well as one of arsenic and potassium, thus making more complete a series of double salts, comparable with the well known alums.

I first made the double chloride of antimony and potassium, then boiled it with concentrated sulphuric acid for eight hours, on cooling well crystallized needles separated out, on the addition of water instead of behaving like the corresponding bromine compound, it immediately broke down into acid antimony sulphate.

A second sample of the double chloride was heated for two days with concentrated sulphuric acid, on cooling the same crystalline mass appeared, and on the addition of water acted as before.

A third sample was heated for eight hours with concentrated sulphuric acid, and in-





dead of trying to crystallize the mass.  
 The excess of acid was boiled off, and the  
 salt placed on a porous plate to dry; by  
 this treatment the salt absorbed moisture  
 from the air and gradually changed into  
 basic antimony sulphate. It was next  
 placed in a vacuum over soda lime  
 and caustic potash; at the end of one  
 month it was fairly dry, although the excess  
 of acid had not entirely disappeared.

An analysis was made which gave 17.9  
 per cent antimony and .78 per cent potas-  
 sium or a ratio between the atoms of  
 antimony and potassium of .498 to .0669  
 instead of 1 to 1.

Further investigation of this salt was given  
 up as it was found impossible to get  
 the salt pure enough for exact analysis.  
 However the work done tends to show the



non-existence of a salt of the composition  $(\text{Si-SO}_4)_2$  analogous to  $(\text{B-SO}_4)_2$ .

This is not surprising since antimony is a much weaker base than bismuth and has greater acid properties, hence we can trace a gradual gradation: - in ordinary alum  $\text{KAl(SO}_4)_3$  we have great stability especially towards water with bismuth-oxysulphate on the other hand we find a tendency for it to break down on boiling with water, while in the case of antimony no double salt  $(\text{Si-SO}_4)_2$  can be obtained.

Arsenic having still greater acid properties will probably 'act like antimony' and show no signs of forming a double sulphate. It would be interesting to see whether an analogous compound containing iron could be made.





## Tri-rubidium Chloro-rismuthite



The only work on the double chlorides of isomuth and rubidium was done by Richard Goëffroy<sup>9</sup> who published his results in 1875<sup>10</sup>, in which he describes as well as gives complete analyses of the salt  $\text{Rb}_3\text{BiCl}_6$  ( $\text{BiCl}_3 \cdot 3\text{RbCl}$ ) which forms a marked exception to the law regarding the constitution of the double halides. As many of the salts described by Goëffroy, which have appeared as exceptions to the law, have by subsequent work been shown not to exist, it was deemed advisable to carefully investigate this double chloride and determine first, whether or not it had the composition  $\text{Rb}_3\text{BiCl}_6$ ,

9. Berchtes 8, 9



secondly to ascertain whether by the further addition of bromine or rubidium chloride a salt could be formed with a greater or less percentage of bromine, similar to the salts obtained in the case of potassium.

His description of the salt is briefly this:

"By evaporation of a hydrochloric acid solution of bromine chloride and rubidium chloride beautiful crystals separate out."

His analysis as follows:

.1535 gram salt gave .191 gram  $\text{AgCl}$  = .0473 gram  $\text{Cl}$

.1535 " " " .036 "  $\text{Bi}_2\text{O}_3$  = .03088\* "  $\text{Bi}$

.423 " " " .707 "  $\text{Rb}_2\text{FeCl}_6$  = .2077 "  $\text{Rb}$

Calculated for  
 $\text{BiCl}_3 \cdot 6\text{RbCl}$

Found

$\text{Bi}$	20.00	20.120
$\text{Cl}$	30.72	30.803
$\text{Rb}$	49.28	49.110

\* A miscalculation, should be .032274 gram  $\text{Bi}$



In order to give the best chance for the formation of this salt, cerium chloride was dissolved in a little cold dilute hydrochloric acid and drop by drop to this was added a hydrochloric acid solution of cerium chloride: thus the presence of a large excess of cerium chloride gave the most favorable opportunity for the formation of a salt containing six atoms of cerium if formed at all.

On the addition of the slightest quantity of cerium chloride, a voluminous crystalline precipitate was immediately formed, no evaporation being necessary.

Godeffroy states that there is no precipitate formed when solutions of cerium and cerium chlorides are mixed.

A small quantity of this precipitate was removed, dried on a porous plate and





analyzed with the following results.

.1884 gram salt gave .0644 gram  $\text{Bi}_2\text{O}_3 = .057734$  gram Bi  
 .1427 " " " .0761 "  $\text{RbCl} = .053772$  " Rb  
 .1999 " " " .2551 "  $\text{AgCl} = .0630607$  " Cl

Calculated for		Found
$\text{BiCl}_3 \cdot 3\text{RbCl}$		
Bi	30.72	30.65
Rb	37.84	37.68
Cl	31.42	31.54

On heating a sample of this salt for 2 hours at  $110^\circ$  it lost in weight not slightly giving only .2 percent loss, which was probably due to incomplete drying.

Thus this analysis of the precipitate goes to show that it has the composition  $\text{Rb}_3\text{BiCl}_6$  ( $\text{BiCl}_3 \cdot 3\text{RbCl}$ ) and not  $\text{Rb}_6\text{BiCl}_9$  ( $\text{BiCl}_3 \cdot 6\text{RbCl}$ ).

Another portion of the precipitate was dissolved in moderately concentrated hydrochloric



nic acid and the solution evaporated, when beautiful transparent crystals separate out, which on the addition of concentrated hydrochloric acid become opaque. These crystals are diamond-shaped, very regular in form, and similar to those of the potassium salt  $K_2B_4Cl_5 \cdot 2H_2O$ , but without the opposite angles cut off. The crystallizing power of this salt is weak and consequently the crystals are of small size but quite uniform.

These crystals were dried on porous plates and then pressed between drying paper and on analysis gave the following results:

I	.1552 gram salt gave .0536 gram $B_2O_3$ = .048042 gram $B_2O_3$
II	.2132 " " " .0734 " $B_2O_3$ = .065803 " $B_2O_3$

---

I	.1835 gram salt gave .0985 gram $RbCl$ = .06961 gram $RbCl$
II	.1609 " " " .0860 " $RbCl$ = .060767 " $RbCl$

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=  
 .1349 gram salt gave .1777 gram AgCl = .043927 gram Cl  
 II  
 .2093 " " " .2670 " AgCl = .066002 " Cl

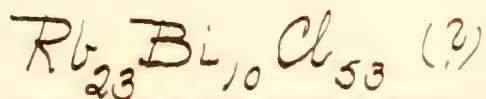
	Calculated for	Found	
	$BiCl_3 \cdot 3R + Cl$	I	II
Bi	30.72	30.97	30.86
R	37.84	37.93	37.76
Cl	31.42	31.49	31.53

The recrystallized precipitate when heated to  $110^\circ$  for 2 hours lost but slightly in weight, showing there is no water of crystallization in the salt: the decrease being due to insufficient drying, probably the presence of a little hydrochloric acid. This salt dissolves undecomposed in dilute hydrochloric acid, and on evaporation of the solution always crystallizes out in the same form. Water decomposes it with the formation of basic bismuth chloride and nitric-



um chloride.

Other attempts to obtain the salt of Godfrey were made by using a cold concentrated solution of rubidium chloride, and a cold dilute solution of bromuth chloride, also hot solutions were used, but without any success - the salt crystallizing out always being  $Rb_3BiCl_6$ .



Since with compounds of stannous chloride and potassium chloride, we get more than one salt, namely  $SnCl_2 \cdot KCl \cdot H_2O$  and  $SnCl_2 \cdot 2KCl \cdot 2H_2O$ , and with bromuth



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chloride and potassium chloride we find  $\text{BiCl}_3 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$  and  $\text{BiCl}_3 \cdot \text{KCl} \cdot \text{H}_2\text{O}$  so it was thought possible to obtain other double chlorides of bismuth and rubidium, containing a greater percentage of bismuth in the molecule by the addition of bismuth chloride to a solution of the salt  $\text{Rb}_3\text{BiCl}_6$  in hydrochloric acid.

When bismuth oxide and rubidium chloride are mixed in the proportion of one molecular weight of the former to two (2) of the latter and the mixture dissolved in dilute hydrochloric acid and evaporated, there separates out a salt crystallizing in most varied forms, resembling shapes of snow crystals, which however on standing change and assume the form of hexagonal plates.

These crystals are transparent, quite small





but very regular in habit.

This salt was obtained in such small quantities that purification by crystallization was impossible; in fact when recrystallized from hydrochloric acid it passes over into the compound  $Rb_3BiCl_6$ ; it can however be recrystallized from a solution of bromine chloride.

An analysis of this salt, sharp enough to give a decided formula could not be made, owing to its probable impurity due to the impossibility of purifying it by repeated crystallization.

The following results were obtained:

I	.1563 gram salt gave .0603 gram $Bi_2O_3$ = .0540589 gram Bi
II	.2483 " " " .0973 " $Bi_2O_3$ = .0872299 " Bi

I	.1563 gram salt gave .0719 gram $RbCl$ = .0508045 gram Rb
II	.2483 " " " .1138 " $RbCl$ = .0814909 " Rb



I  
 .1525 gram salt gave .1956 gram AgCl = .0483523 gram Cl  
 II  
 .1992 " " " .2551 " AgCl = .0630607 " Cl

Calculated for		Found	
10B <sub>2</sub> Cl <sub>3</sub> .23RbCl		I	II
B	35.11	34.58	35.17
Rb	33.17	32.50	32.83
Cl	31.72	31.74	31.66

from analysis I the calculated ratio between the bromine and rubidium atoms is 1 to 2.296 and from analysis II, 1 to 2.275 and the formula which would seem most probable, in view of these facts is Rb<sub>23</sub>B<sub>10</sub>Cl<sub>53</sub> or 10B<sub>2</sub>Cl<sub>3</sub>.23RbCl. Were it not for certain facts along a similar line of work undertaken by Mr. C. E. Saunders, under the direction of Prof. Rensselaer the latter formula would seem highly unportable. This gentleman working on the double chlorides of antimony and



rubidium, obtained a salt, crystallizing in the same form, the analysis of which gave a ratio between the bromine and rubidium atoms of 1 to 2.296. (mean of three analyses).

The one fact which goes to establish these results as most exact is that this double salt of antimony and rubidium can be recrystallized from hydrochloric acid without change of composition, and it is into this salt that all double chlorides of antimony and rubidium change, when subjected to recrystallization from dilute hydrochloric acid.

The results which Mr Saunders obtained were from the analyses of the salt which had been purified by recrystallization five times.

Since bromine is so closely related to anti-





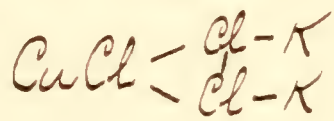
mony and the work on the double Chloride of the latter with rubidium shows the existence of a salt of the probable composition  $10\text{SrCl}_2 \cdot 23\text{RbCl}$ , it is not surprising that a similar compound of rosmuth should be formed; from this fact and the results actually obtained by me in the analysis of the salt above described, I feel justified in assigning to this compound the formula  $\text{Ro}_{23}\text{Bi}_{10}\text{Cl}_{53}$ .

With the existence of this and the similar antimony salt the view that "halogen atoms can play the same part as linking oxygen atoms" must be slightly modified. This modification is fully set forth in Mr Saunders's dissertation for the degree of Doctor of Philosophy. Johns Hop. Univ. University, 1891.

The view this gentleman takes is that in



The compounds  $10\text{SbCl}_3 \cdot 23\text{RbCl}$  come of the chlorine atoms may be assumed to be in groups of three with three for valencies, and that with this assumption not only can these two compounds be explained, and brought into harmony with the other double halides, but the compound  $\text{CuCl} \cdot 2\text{KCl}$  which has always stood out as a marked exception finds a partial explanation: according to this view it would have this structure



This salt ( $\text{Rb}_{23}\text{Bi}_{10}\text{Cl}_{33}$ ) dissolves to a clear solution in dilute hydrochloric acid, from which on partial evaporation, there crystallizes out the salt  $\text{Rb}_3\text{BiCl}_6$ , which appears to be the one that these elements always assume under ordinary conditions. In water this salt is decomposed with the formation of basic bromine chloride.



## Mono-rubidium Chloro-bromite



Besides the compounds  $\text{Rb}_3\text{BiCl}_6 (\text{BiCl}_3 \cdot 3\text{RbCl})$  and  $\text{Rb}_{23}\text{Bi}_{10}\text{Cl}_{33} (10\text{BiCl}_3 \cdot 23\text{RbCl})$  another was obtained, which in all probability corresponds to the mono-rubidium chloro-bromite and has the composition  $\text{RbBiCl}_4 \cdot \text{H}_2\text{O}$ . It was found that when  $2\frac{1}{2}$  molecular weights of bromine oxide were dissolved in concentrated hydrochloric acid, and 2 molecular weights of rubidium chloride were added and the solution evaporated to a syrupy consistency, after a time white hair-like crystals formed and finally the contents of the vessel became almost solid; the beaker in which the salt was formed was turned on its side and the liquid al-





allowed to drain off, after which the  
 crystals were transferred to a porous plate  
 and finally dried between filter papers  
 if the evaporation of the solution is stopped  
 before the liquid becomes sufficiently con-  
 centrated for the formation of these needle-  
 like crystals, there always separates out  
 crystals of the compound  $10\text{BiCl}_3 \cdot 23\text{RbCl}$ ,  
 while on the contrary should the evaporation  
 be carried beyond the point at which the  
 hair-like crystals first form these needles  
 although they are formed do not appear sepa-  
 arate but seem to start from points and  
 form themselves into a solid mass radi-  
 ating from these points as centres.  
 The cerium chloride used in this ex-  
 periment was found on analysis to be slightly  
 impure, containing certainly a slight  
 trace of caesium.



7-  
.2522 gram PbCl gave .2866 gram AgCl = .07084 gram Cl  
= 28.09%.

Theoretical percent of Cl in PbCl = 29.34

The conditions under which this double salt is formed — in a very concentrated solution of bromine chloride — gives little opportunity for the purification of the salts used.

Here this salt formed in dilute acid solution may impurities present in the mercuric chloride might be removed by the difference in solubility of the double salts produced, but being formed in such concentrated solutions where bromine chloride is present in such large excess, and where it appears as if all of both constituents present enter into combination, it is not surprising that if caesium is the impurity in the mercuric chloride, that it would be carried along by both constituents and enter into combination.



This is probably the reason why the analyses of the salt do not correspond to any simple formula although its similar method of formation and appearance to the potassium salt of the composition  $KBiCl_4 \cdot H_2O$ , strongly indicates one with the hint that it most probably has the composition  $PbBiCl_4 \cdot H_2O$ . The results of the analyses of three different samples are as follows:

Sample A

I  
 .275 gram salt gave .0022 gram  $Bi_2O_3$  = .055762 gram Bi  
.1223 " " " .0598 "  $Bi_2O_3$  = .0536107 " Bi

Sample B

I  
 .1815 gram salt gave .0743 gram  $Bi_2S_3$  = .000640 gram Bi  
.1263 " " " .0643 "  $Bi_2O_3$  = .0576449 " Bi  
.4108 " " " .2315 "  $Bi_2S_3$  = .1880243 " Bi

Sample C

I  
 .250 gram salt gave .1212 gram  $Bi_2S_3$  = .0984385 gram Bi  
.1666 " " " .0940 "  $Bi_2S_3$  = .0763468 " Bi





Sample A

I  
 .1275 gram salt gave .0394 gram  $RbCl = .02784$  gram  $Rb$ .

II  
 .1223 " " " .0379 "  $RbCl = .02678$  "  $Rb$

Sample B

I  
 .1315 gram salt gave .0408 gram  $RbCl = .028829$  gram  $Rb$

II  
 .1263 " " " .0408 "  $RbCl = .028829$  "  $Rb$

Sample C

I  
 .1666 gram salt gave .0520 gram  $RbCl = .036842$  "  $Rb$ .

Sample A

I  
 .1204 gram salt gave .1564 gram  $AgCl = .038652$  gram  $Cl$

II  
 .1829 " " " .2379 "  $AgCl = .0588088$  "  $Cl$

Sample B

I  
 .1203 gram salt gave .1562 gram  $AgCl = .0386126$  gram  $Cl$

II  
 .1739 " " " .2261 "  $AgCl = .0558919$  "  $Cl$

Sample C

I  
 .2189 gram salt gave .2848 gram  $AgCl = .0704025$  gram  $Cl$

II  
 .2578 " " " .3350 "  $AgCl = .082812$  "  $Cl$



Sample A

.4347 gram salt lost .0110 gram  $H_2O$  heated for 2 hrs.  $105^\circ$

Sample B

.4151 gram salt lost .0043 gram  $H_2O$  heated for 2 hrs.  $105^\circ$

Sample C

.4086 gram salt lost .0067 gram  $H_2O$  heated for 2 hrs.  $105^\circ$

.1957 " " .00295 "  $H_2O$  " " 2 "  $105^\circ$

Calculated for			Sample A		Found			Sample C	
$Pb-Bi-Cl_4 \cdot H_2O$ : $Pb-Bi-Cl_4$			I	II	I	II	III	I	II
Pb	45.89	47.79	43.73	43.83	45.89	45.64	45.77	45.78	45.82
Bi	18.84	19.62	21.83	21.89	21.29	21.57	—	—	—
Cl	31.29	32.58	32.10	32.17	32.09	32.14	—	32.16	32.11
$H_2O$	3.97	—	2.53	—	1.03	—	—	1.64	1.50

The bromine in analyses I and III sample B and I and II sample C was determined as the sulphide - while that in I and II sample A and II sample B was calculated from the oxide.

It will be seen on comparing the results cal-



culated for  $RbB\cdot Cl_4 \cdot H_2O$  with the percentages found that while there is a discrepancy in the case of rubidium and water, the percentages for bromine and chlorine are close, and as I previously stated, on account of the great similarity between it and the compound  $KB\cdot Cl_4 \cdot H_2O$  I am satisfied to state that if the rubidium chloride had been perfectly pure the results obtained on analysis would have been extremely close to the calculated percentages for  $RbB\cdot Cl_4 \cdot H_2O$ . The salt, as is the case with the other salts of bromine and rubidium, is decomposed by water, it yields a clear solution when treated with dilute hydrochloric acid, from which on slight evaporation there separates the salt  $B\cdot Cl_3 \cdot R\cdot Cl$ .

All efforts to obtain salts composed of bromine and rubidium chlorides, other than have





here been described, have been fruitless.  
From these facts it appears to follow that  
the salt  $\text{BiCl}_3 \cdot 6\text{POCl}_3$ , described by Godefr<sup>1</sup>,  
does not exist, and cannot under <sup>the</sup>  
most favorable conditions — in the presence  
of a large excess of nitrdum chloride — be  
formed.

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### Caesium-bismuth Chlorides.

As with nitrdum so with caesium Godefr<sup>12</sup> describes a salt of the composition  
 $\text{BiCl}_3 \cdot 6\text{CsCl}$  and to determine whether such  
a compound exists, was the following work  
undertaken. The Caesium Chloride



for this investigation was obtained from the  
 factory of Theodor Schuchardt. Görlitz. Es  
 on analysis it was found to be very im-  
 pure, containing most probably rubidium  
 and potassium; so before beginning  
 the investigation of this double chloride, it  
 was necessary to purify this salt.

The method<sup>13</sup> employed depended on the differ-  
 ence in solubility of the double salts of an-  
 timony-rubidium chloride, and antimony-  
 caesium chloride, the former being soluble  
 in concentrated hydrochloric acid, the latter  
 not. The caesium chloride was dissolved  
 in moderately concentrated hydrochloric acid  
 and a solution of antimony chloride in  
 hydrochloric acid added until it ceased forming  
 a precipitate; this was allowed to stand un-  
 til clear when the supernatant liquid was  
 poured off; concentrated hydrochloric acid was



added to the precipitate, in which case any  
sublimum-antimony chloride present, would  
dissolve. This liquid was poured off, when the  
precipitate remaining should contain only  
caesium-antimony chloride. This was dis-  
solved in no concentrated hydrochloric acid.  
Then hydrogen sulphide was passed in, for a  
long time as the large quantity of acid  
used to dissolve this salt prevents the com-  
plete precipitation of the antimony at once.  
The antimony sulphide was filtered off, and  
the filtrate containing the caesium chloride  
was evaporated to dryness in a platinum  
dish. If a glass or porcelain vessel is used  
some alkali from the glass will be dis-  
solved to drive off the last trace of hydrochloric  
acid, it was heated to  $130^{\circ}$  in an air  
bath. The caesium chloride thus treated  
was found to be much purer than that





with which I started, yet a second purification seemed advisable; the result of which gave me a small quantity of the salt which analyzed as follows:

.1711 gram  $\text{CsCl}$  gave .1470 gram  $\text{AgCl}$  = .0363384 gram  $\text{Cl}$   
 = 21.23 percent theoretical percentage of  $\text{Cl}$

in caesium chloride = 21.05 This is probably as pure as caesium chloride can be obtained by this method: The quantity of the salt would not warrant a third purification.

Godeffroy<sup>4</sup>, in his description of the salt  $\text{BiCl}_3 \cdot 6\text{CsCl}$  says he obtained, by mixing solutions of bromine and caesium chloride in hydrochloric acid, a precipitate which is difficultly soluble in hydrochloric acid and his analysis is as follows

.900 gram salt gave .801 gram  $\text{AgCl}$  = .213 gram  $\text{Cl}$ .

.900 " " .154 "  $\text{Bi}_2\text{O}_3$  = .38 "  $\text{Bi}$

.510 " " .788 "  $\text{Cs}_2\text{P}_2\text{Cl}_6$  = .3095 "  $\text{Cs}$ .



Calculated for		Found
$\text{BiCl}_3 \cdot 6\text{CoCl}_2$		
Cl	24.10	23.67
Bi	10.68	10.67
Co	60.22	60.09

Following these directions for making this salt, To a saturated solution of Calcium Chloride in dilute hydrochloric acid was added drop by drop a solution of bismuth chloride when a voluminous precipitate difficultly soluble was formed. A close examination of the precipitate shows the presence of two distinct kinds of crystals.

In order to follow Godfrey's direction and obtain his salt, this precipitate as it stood was analyzed.

A sample of it dried on a porous plate and finally between filter paper, gave the results.

.171 gram salt gave .0701 gram  $\text{Bi}_2\text{S}_3$  = .0569382 gram Bi

.081 " " .0782 "  $\text{Bi}_2\text{S}_3$  = .053517 " Bi









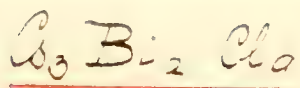
as the impurity.

This precipitate dissolves easily in warm dilute hydrochloric acid one of the salts with apparently more ease than the other, so as one could expect it is just an easy matter to separate and obtain them in pure condition by recrystallization.

On evaporation of a solution of the precipitate in hydrochloric acid, the more compact looking crystals, which settled to the bottom of the precipitate formed yellowish elongated pyramids, while the others, which are the more easily soluble assume a flaky appearance (these are white or colorless). After separation each lot was recrystallized three times from dilute hydrochloric acid, and although but a small quantity of each was obtained they appeared quite pure and gave excellent results in analysis.

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That part of the precipitate, formed by mixing solutions of bismuth and caesium chlorides in hydrochloric acid, which on crystallization forms elongated pyramids, yellow in color, has the composition  $\text{Co}_3\text{Bi}_2\text{Cl}_9$ , as shown by the following analysis.

.587 gram salt gave .072 gram  $\text{Bi}_2\text{S}_3$  = .0587787 gram Bi

.587 " " " .0708 "  $\text{CoCl}$  = .0558966 " Co

.1390 " " " .1586 "  $\text{AgCl}$  = .0392059 " Cl

Calculator for  
 $2\text{BiCl}_3 \cdot 3\text{CoCl}_2$

Found

Bi 36.68

36.84

Co 35.18

35.22

Cl 28.13

28.20

This salt on treatment with water decomposes with the formation of oxychloride of bismuth and caesium chloride: in acid



dilute hydrochloric acid it is difficultly sol-  
 ule, but dissolves readily when warmed.  
 Both the formation of this salt is the similar-  
 ity between the elements bromine and anti-  
 mony again shown, as the chloride of the  
 latter with caesium chloride only forms a  
 salt of the composition  $\text{Cs}_3\text{Sb}_2\text{Cl}_9$

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### Tri-caesium Chloro-bromuthide.



That part of the precipitate which crystallizes  
 in thin transparent plates has the com-  
 position  $\text{Cs}_3\text{BiCl}_6$

The results obtained on analysis of this salt  
 are as follows:





I  
189 gram salt gave .0376 gram  $B_2S_3$  = .0305387 gram  $B_2$

II  
1730 " " .0544 "  $B_2S_3$  = .044806 "  $B_2$

I  
II  
1730 gram salt gave .1063 gram  $CoCl$  = .08392385 gram  $Co$

I  
081 gram salt gave .0860 gram  $AgCl$  = .0212592 gram  $Cl$

	calculator for $B_2Cl_3 \cdot 3CoCl$	Found	
		I	II
$B_2$	25.37	25.58	25.53
$Co$	48.67	—	48.51
$Cl$	25.95	26.08	—

Through an accident the determination of caesium in analysis I was lost.

The behavior of this salt is much like that of the combination  $Co_3B_2Cl_9$ ; it is difficultly soluble in dilute hydrochloric acid but when warmed dissolves easily.

With the double chlorides of rubidium and



caesium with bromine, it was so difficult to obtain the compounds well crystallized that an investigation into their crystallographic properties was not undertaken.

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### Conclusion

The principal results of this investigation are these:

I Of the three chloro-bromides of potassium only the one described by Jacqueline Laro (B.Cl<sub>3</sub>.2KCl.2H<sub>2</sub>O)<sup>15</sup>; while one of the composition B.Cl<sub>3</sub>.KCl.7H<sub>2</sub>O, not described in the literature, can be formed under certain conditions.

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<sup>15</sup> Ann. chim. phys. 66, 113.



II No salt of the composition  $Rb_6B_2Cl_9$  exists, but from the chlorides of rosmuth and mixed with the following three salts can be formed

$$Rb_3B_2Cl_6 \quad Rb_{23}B_{10}Cl_{53} \quad RbB_2Cl_4 \cdot H_2O$$


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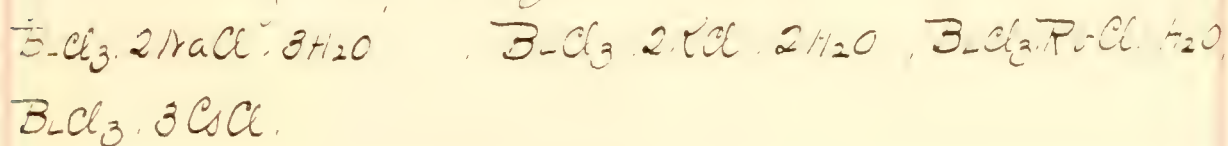
III The salt, to which Godeffroy ascribes the composition  $B_2Cl_3 \cdot 6CsCl$  is a mixture of the two salts  $Cl_3B_2Cl_6$  ( $B_2Cl_3 \cdot 3CsCl$ ) and  $Cl_2B_2Cl_9$  ( $2B_2Cl_3 \cdot 3CsCl$ ), and cannot under any possible circumstance be formed

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IV All double chlorides of rosmuth with the alkali metals are decomposed by water.

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I As the atomic weight of the alkali in combination with rosmuth increases, the amount of water of crystallization decreases thus:







II Of the 2 atoms to the law of combination in double halides, only the now dict.  $\text{CuCl} \cdot 2\text{KCl}$  and  $\text{CdCl}_2 \cdot 4\text{KCl}$  all most one on these two compounds show their composition to be expressed in these formulae.

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## Biographical Sketch.

The author of this dissertation, Charles Pliny Bringham, was born February 3, 1857 in Bath, near Maryland. He prepared for college at the "University School for Boys" in that city. In the fall of 1885 he entered the Johns Hopkins University as an undergraduate; after following the course in Chemistry & Physics graduated with the degree of Bachelor of Arts in June 1888.

In the following fall he entered the graduate department where he has pursued the study of Chemistry, with mineralogy and geology as subsidiary subjects.

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